Seaweed Biopolymers as Additives for Unfired Clay Bricks

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Abstract

Unfired clay bricks are an environmentally friendly alternative to conventional masonry materials such as fired bricks and concrete blocks but their use is currently limited by their relatively poor mechanical and durability properties. While products like cement and lime are commonly added to earthen materials in an effort to improve their physical performance, these additives can also have a negative influence on the overall environmental impact. The purpose of this research is to investigate the use of alginate, a natural and renewable biopolymer obtained from brown seaweeds, as an admixture for unfired clay blocks. A total of 5 different alginates have been investigated and combined with 3 soil compositions to create prototype specimens which have then been characterised and compared in relation to flexural and compressive strength, microstructure, abrasive strength and hygroscopic behaviour. The results demonstrate that improvements in mechanical strength are dependent on the type of alginate used and the composition of the soil. The greatest increase in compressive strength is achieved using an alginate sourced from the *Laminaria Hyperborea* seaweed and offers a value more than double that of the equivalent control specimen. Increases in the alginate dosage do not necessarily lead to an increase in strength suggesting that there is an optimum concentration at which strength improvement is most effective.

Keywords: biopolymer; alginate; seaweed; clay; brick; CEB; adobe; polysaccharide

1. Introduction

Material selection plays a vital role in determining the environmental performance of a building (Takano et al., 2014). This requires consideration of the resources and energy consumed during manufacture as well as the influence on operational aspects such as indoor air quality and the overall energy efficiency of the building fabric. Life-cycle aspects such as transportation, maintenance requirements and the opportunities for re-use or recycling at the end of the building's useful lifespan also play an important role. It has also been argued that as efforts to improve energy-efficiency and building performance increase in line with legislative targets (European Commission, 2010), the environmental impact of building materials will become more significant (Thormark, 2002; Sartori and Hestnes, 2007;Fouquet et al., 2015). As a consequence of this growing environmental awareness, research into alternative building materials which incorporate natural, biological compounds as opposed to non-renewable and petroleum based materials is also increasing. Furthermore, the development of new bio-composite products which incorporate bio-based components either in the form of natural fibres or binders is also being investigated for use within the construction industry. Indeed a recent review by Coulson and Fuller (2012) demonstrated that biological products such as cellulosic materials and polysaccharides, as well as various oils and proteins, could be used in various construction applications including adhesives, masonry units and panel products. In addition, agro-industrial waste and non-food crops have been identified as particularly valuable sources of useful organic materials (Van Wyk et al., 2012).

The purpose of this study is to investigate the use of a biopolymer obtained from seaweed, within a composite building product. This research builds on a previous study by Galán-Marín et al. (2010) which utlised alginate as a binder within an unfired clay brick. Whilst the authors reported improvements in strength upon the addition of the biopolymer, there was a requirement for further investigation into the role of the alginate component in the product, including the importance of the chemical composition of the seaweed sources, as well as the impact of the alginate upon properties other than mechanical strength. This research project has therefore investigated a wide range of alginate types with three soil types and performed additional characterisation tests in order to assess more rigorously the feasibility of using this abundant material in construction applications.

2. Literature Review

2.1. The Use of Biopolymers in Construction

Biopolymers are polymeric substances which are derived from natural sources, the majority being carbohydrates from plant and algal feedstocks. These carbohydrates represent half of all the organic carbon in the world and polysaccharides constitute over 90% of these compounds (BeMiller, 2000). Polysaccharides are therefore readily available materials which can be obtained

at a low cost from renewable sources and consequently have been adopted within in a wide range of applications including agriculture, the food industry, textile and paper manufacturing as well as more recent developments like biomedical materials and bio-plastics (Nussinovitch, 1997). There are various examples of biopolymers being used in building materials and in fact such organic materials were used widely during the Roman era where locally available natural products would be used to enhance the properties of concrete and masonry materials (Plank, 2005;Quagliarini and Lenci, 2010). Today biopolymers like lignosulphonate, derivatives of starch and cellulose and various water-soluble polysaccharides are used in a wide range of construction applications including concrete, mortars and grouts, plasters, plasterboards, paints and oil well drilling fluids (Plank, 2005; Vieira et al., 2005).

2.2. Biopolymers as additives for Unfired Clay

Unfired earth is a traditional building material which has been used for thousands of years but has witnessed a resurgence in recent decades, particularly within Europe, the USA, Australia and New Zealand, owing to its excellent environmental credentials in comparison to contemporary alternatives (Pacheco-Torgal and Jalali, 2012). For example, in energy terms, the elimination of the kiln-firing process normally used in ceramic products means that unfired clay has a significantly lower embodied energy than fired bricks. In fact it has been reported that unfired clay bricks require only 14% of the embodied energy of ceramic brick and 25% of the energy needed to produce lightweight concrete (Morton, 2006). Earth is also a ubiquitous and abundant resource which can usually be sourced locally and cost efficiently and, as an inert, natural product, it can be easily returned to the natural ecosystem at the end of its useful life. Unfired earth can also offer further benefits such as improving indoor air quality and thermal comfort for inhabitants when exposed internally. For example, clay's hygroscopicity and excellent moisture buffering properties can help to maintain a healthy level of humidity within buildings, thereby reducing the risk of mould growth (Hall and Allinson, 2009;McGregor et al., 2014b). In addition, since unfired clay is a high density material, it also provides thermal mass within the building structure which acts as a passive form of heat storage as well as providing acoustic insulation (Morton, 2008). These thermal and moisture buffering properties also help to reduce loads on heating and ventilation systems and can have an important impact on overall operational performance (Rode and Grau, 2008). Unfired clay is therefore an attractive material for use in internal environments, particularly when used in passive design strategies.

There are however still a number of disadvantages to building with earth which limit its application. These include poorer durability, particularly in relation to moisture sensitivity, as well as relatively lower load bearing capacities (Walker, 1995;Oti et al., 2009). There is therefore a renewed incentive to improve these disadvantageous characteristics in order encourage more widespread use of unfired earth in buildings. This evidenced by the growing amount of literature in compressed stabilised earth blocks and stabilisation techniques for rammed earth (Walker and

Stace, 1997; Walker, 2004; Morel et al., 2007; Heath et al., 2009; Lawrence et al., 2009; Deboucha and Hashim, 201; Oti and Kinuthia, 2012; Miqueleiz et al., 2013). The majority of contemporary investigations have focused on the use of additives such as Portland cement and lime. However, there is currently some debate as to whether the resulting stabilized materials are necessary given the rich heritage of buildings constructed using un-stabilised earth (Morel et al., 2013) .For instance, existing constructions which do not make use of stabilisers have stood for over a century within relatively wet climates in Europe (Aubert et al., 2015a).

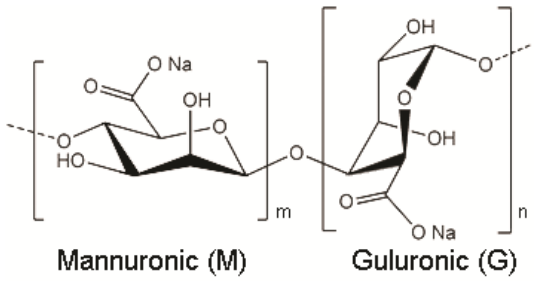
Within the UK however, in order to be considered as a contemporary material which can compete with conventional fired bricks and concrete, thinner wall sections and hence greater structural capacity is required (Heath et al., 2012). The use of strength improving additives may therefore be necessary in order to meet the demands of modern building regulations. Furthermore, some soils type can lack sufficient cohesiveness to be suitable for earth building unless appropriately modified. There are also concerns regarding the moisture sensitivity of unstabilised materials, and whilst the inclusion of cement or bitumen for example will improve the wet strength of a material, conventionally stabilised earth has various disadvantages. For instance, the use of both cement and lime can lead to significant increases in embodied energy and CO_2 emissions (Worrell et al., 2001;Hammond and Jones, 2008). It is therefore also important that specified stabilisers do not diminish the advantageous properties of unfired earth. Consideration of the effect on factors such as cost, recyclability and humidity regulating properties should therefore also be taken into account. For instance, the addition cement and lime has also been shown to reduce vapour permeability (McGregor et al., 2014a). There are therefore growing efforts to find alternatives to conventional stabilisers which are not only environmentally friendly but which also retain the beneficial properties of natural clay.

Biopolymers offer a potential solution to this challenge in that they are organic materials which can be used to modify the properties of clays, and potentially enhance particle binding. Polysaccharides exist naturally in soils where they play an important role as binding agents contributing to soil stability (Theng, 2012a). It is for this reason that various biopolymers have been investigated as potential stabilisers for agricultural soils (Emerson, 1956; Orts et al., 2007). In the case of building materials, there is also evidence of various plant-based products such as vegetable oils (Heaton et al. ,2014;Ogacho et al., 2003; Balo and Yucel, 2013), tannins gums and resins (Ruskulis, 2002) as well as various animal based polymers (Eires et al., 2013; Beas, 1991) being successfully used to modify the properties of raw earth. Whilst there is clearly the potential for natural biopolymers to consequently be used as binding agents within masonry materials, additional research into their desired properties and commercial viability is required.

2.3. Alginate

Alginate is the collective term for the salts of alginic acid which are obtained from the cell walls of brown macro-algae, otherwise known as *Phaeophyceae*. These salts, usually in the form of sodium or potassium, contribute to 20-60% of the dry matter of the algae (Rehm, 2009). Alginate polymers are also a form of hydrocolloid, a hydrophilic polymer which can be mixed with water to form a gel (Burey et al., 2008), which unlike some other polysaccharides does not depend on temperature induced gelation (Lencina et al., 2013). Alginate is therefore currently used in numerous stabilising, binding and gel-forming applications and found in many commercial products ranging from processed foods and textile dyes to dental impression materials and pharmaceutical products (Draget et al., 2009). Figure 1 shows the structure for sodium alginate $(C_6H_7NaO_6)_n$ which is a block co-polymer consisting of (1-4)-linked β-D-mannuronic acid and α-L-guluronic acid residues. The ratio and sequence of these components, otherwise known as M and G blocks, vary within the polymer chain (Rehm, 2009). This variation depends on a number of factors including the type and age of the algal species from which the alginate is sourced, the season during which it is harvested and the general growing conditions and climate. In addition, different parts of the same seaweed have also been found to offer different polymer compositions. For example, in the *Laminaria Hyperborea* seaweed it has been shown that the stem will have a much higher G content than the frond, the leaf like component, due to the fact that the stem part requires a stronger gel structure (Draget et al., 2009).

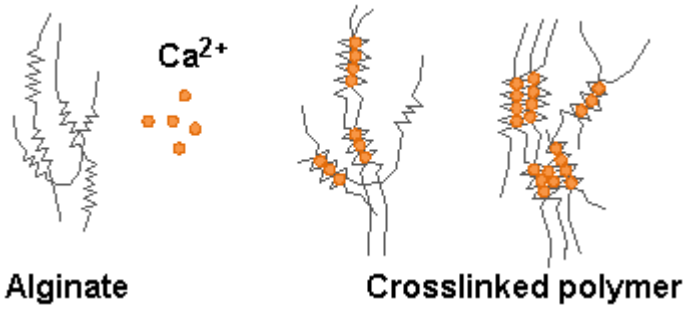
Fig. 1 Alginate Polymer Structure



Alginates can form cross-linked gels through iontropic gelation. This occurs when a soluble form of alginate, usually sodium alginate, is converted to an insoluble gel through the introduction of divalent metal cations such as Ca^{2+}. For alginates, this gel-forming mechanism is commonly described by the 'egg-box model' (Grant et al., 1973). This involves cooperative binding in water where interactions between the G blocks of the negatively charged alginate polymer and the positively charged ions create chain to chain associations as illustrated in Figure 2. This is due to the formation of junction zones between two or more chains where the cations sit within the buckled parts of the molecule, like eggs in an egg box. During the gelation process, the number of chain to chain associations increases, eventually leading to the formation of a continuous network

(Rees and Welsh, 1977). Consequently, the gelation process can be influenced by factors such as the M/G ratio and sequencing of the alginate, the cation type and dosage, the alginate molecular weight and the molecular weight distribution (Funami et al., 2009).

Fig 2 Schematic of the 'egg-box' model



2.4. Alginate as an additive for unfired masonry

As a readily available, biocompatible and relatively low cost biopolymer, alginate has the potential to be used as an alternative to traditional stabilisers. Composite materials which combine sodium alginate and clays are currently being investigated in applications as diverse as drug delivery (Pongjanyakul and Puttipipatkhachorn, 2007; Wang et al., 2013; Iliescu et al., 2011), heavy metal adsorption (Li et al., 2011) and nano-composite films (Yang et al., 2009). Several studies have also discussed the use of alginate in agricultural applications where the alginate-clay interactions are used to increase the stability of soil aggregates or to aid plant growth (Quastel and Webley, 1947; Emerson, 1956; Schneider, 1977; Orts et al., 2007; Bernu et al., 2010). In looking specifically at the use of alginate as an additive for masonry materials however, a much more limited range of studies have been conducted. Although a few authors have mentioned the use of seaweed in building products (Minke, 2006; Han et al., 2008; Achenza and Fenu, 2006; Lee et al., 2008), only a handful of papers have investigated the specific use of alginate.

As previously mentioned, the most detailed investigations to date are those conducted by Galán-Marín et al. (2010) and subsequent studies (Galan-Marin et al., 2012; Galán-Marín et al., 2013; Rivera-Gómez et al., 2014) which discuss the use of alginate, in combination within lignin and natural or synthetic fibres, as additives for unfired clay bricks. Maximum compressive strengths of over 4 N/mm^2 are reported and it is claimed that this material could offer a suitable replacement for convential internal walling systems. A life-cycle analysis (LCA) study has also shown that these bricks may have a lower embodied energy than fired materials and a lower Global Warming Potential (GWP) than both fired bricks and reinforced concrete (Galán-Marín et al., 2015). Although the authors observed compressive strength improvements upon the addition of the alginate solution alone, the main focus of those studies was on the role of the fibrous components.

Furthermore, more recent studies showed variable results when the same alginate was used with alternative soils and different types fibres (Galán-Marín et al., 2013). The type of alginate products used in the studies included both a liquid 'seaweed extract' (Galán-Marín et al., 2010) and a dried alginate powder (Rivera-Gómez et al., 2014) , with the authors concluding that the type of product and the specific alginate-clay interactions required further investigation.

The principal aim of this study was therefore to explore in more detail the role of the alginate component, analysing the specific properties and chemical interactions of the polymer. In the case of the alginate-clay interactions, it is postulated that the addition of alginate will strengthen the existing soil matrix through inter-particle bridging. Indeed other studies have shown that alginate can help to increase the stability of soil aggregates by exchanging with hydroxyl ions (OH^-) at the soil particle surface. This helps to create hydrophilic surfaces and bridges between individual soil particles through calcium or aluminium cations. Quastel and Webley (1947) and Emerson (1956) demonstrated improvement in soil stability upon the addition of sodium alginate, noting the importance of both the molecular weight of the alginate and the specific properties of the soil. A more recent study by Nugent et al. (2009) involving Xanthan gum, another anionic polysaccharide, highlighted the complexities of soil-biopolymer interactions, concluding that variables such as the type and quantity of cations present within the soil, in addition to the viscosity and concentration of the polymers used, can all have a significant influence. Additionally, the authors found that some nano-scale interactions can actually have a negative impact on the overall shear strength of the soil.

Theng (2012b) summarises the main interaction mechanisms for clays and negatively charged polymers like alginate by reporting that although anionic polymers would be expected to show weaker adsorption than cationic or non-ionic polymers (due to the electrostatic repulsion with negatively charged clays) there were certain conditions which help to promote adsorption (Theng, 2012b). Firstly, adsorption can occur in the form of anion exchange which takes place between the negatively charged polymer and the variable charge at the edges of the clay particles. This type of interaction is pH dependent since the edge charges can be positive, negative or neutral depending on the pH conditions. Furthermore the pH of the system also affects the magnitude of the charge on the ionic group of the polymer. A low pH would therefore help to reduce electrostatic repulsion between the two components and potentially promote adsorption. Ligand exchange can also occur between the acidic hydroxyl group of the polysaccharide, such as carboxylic and phenolic groups, and hydroxyl groups of the clay surface (Theng, 2012b). In natural soils, most of the adsorption of organic and humic materials occurs in this way (Gu et al., 1994), particularly in soils which are acidic and have a high content of oxides (Keil and Mayer, 2013). This adsorption mechanism is relatively strong and can reportedly last for over 100 years (Lützow et al., 2006). Another adsorption mechanism occurs where polyvalent, exchangeable cations are present in the form of cationic bridging between the anionic groups of the alginate and the negative surface of the clay. This can take place either directly or through a water bridge (Gu and Doner, 1992). Given the

affinity of alginate for calcium ions and the previously described 'egg-box' crosslinking mechanism, it is likely that the presence of Ca^{2+} ions could help to create electrostatic bridges between the anionic part of the polymer and the clay surface (Yalçın et al., 2002). Other weaker adsorption mechanisms include Van der Waals and hydrophobic interactions and hydrogen bonding (Theng, 2012b).

Overall existing studies agree that interaction between alginate polymers and clay particles can occur through numerous mechanisms and that these interactions may be influenced not only by polymer variables but also by variables in the soil including the concentration and type of clay particles present, the quantity of available cations and the soil pH (Benli et al., 2011). In order to investigate the role of these factors, five different alginate products, of varying viscosities and composition were sourced and combined with three different soil types. The experimental methodology therefore involved firstly characterising the raw materials, manufacturing prototypes of the alginate-clay composite and then measuring and comparing the physical, chemical and mechanical properties of the different specimens. In addition to flexural and compressive strength tests, further characterization tests such as assessments of abrasive strength, hygroscopic behavior and water sensitivity were also conducted in order to determine whether the material would be suitable for further development as a building product.

3. Methodology

3.1. Materials

3.1.1. Soil

The soils used in the study were supplied by Ibstock Ltd and sourced from UK clay quarries. All soils were characterised using standard procedures and their properties are summarised in Table 1. Loss on Drying (LOD) and Loss on Ignition (LOI) was calculated using the methods outlined in BS EN 15935:2012. Soil pH was measured using a 1:5 volume ratio of dry soil to a 0.01 mol/L $CaCl_2$ solution (BS EN 15933:2012). Particle size distributions were obtained using the sedimentation method described in BS 1377-2:1990. Atterberg limits were calculated using the soil thread method for plastic limit and the cone penetrometer method for the liquid limit (BS 1377-2:1990) and the maximum dry density and optimum moisture contents were determined using an adapted version of the procedure outlined in BS 1377-4:199. In this case rather than adopting the standard Proctor method which uses a 1L cylindrical mould and either a 2.5 or 4.5kg rammer, and consequently uses a greater level of compaction than in typical used in earth block production (Mesbah et al., 1999; Kouakou and Morel, 2009), the adapted method used the same rectangular moulds and hand compaction techniques as used to produce the final blocks. Cation exchange capacity and specific surface area were calculated from the Methylene Blue test (BS EN 933-9:2009) and calcium (Ca) contents were obtained by inductively coupled plasma (ICP)

measurements on soil extracts obtained using the aqua-regia method for Total Elemental Ca and a deionised water (DI) extract for the Available Ca.

Table 1 Summary of Soil Properties

Soil Type		**U**	**V**	**W**
pH ($CaCl_2$)		4.8	6.8	6.9
Loss on Drying at 105°C (%)		2.9%	3.9%	2.3%
Loss on Ignition at 550°C (%)		7.5%	8.2%	6.5%
Sand and Gravel	**>0.06mm**	24%	29%	23%
Silt	**0.002–0.06mm**	45%	44%	61%
Clay	**< 2µm**	31%	27%	16%
Soil Classification		Clay Loam	Loam	Silt Loam
Plastic Limit (%)		16.0%	14.6%	15.3%
Liquid Limit (%)		27.3%	27.9%	25.4%
P.I. (%)		11.3%	13.3%	9.9%
Plasticity Classification		CL (lean clay with sand)		
Maximum Dry Density (g/cm^3)		1.82	1.98	1.92
Optimum Moisture Content (%)		16%	18%	14%
Electrical Conductivity (µS/cm)		640	115	169
Cation exchange capacity (meq/100g)		4	5	5
Specific Surface Area (m^2/g)		12.6	20.2	17.6
Total Elemental Ca (ppm)		1670	3910	3460
Available Ca (ppm)		750	2330	1730

Table 2 Summary of Soil Chemical Composition (SEM-EDS)

Element	**Oxide**	**U - Weight %**	**V - Weight %**	**W - Weight %**
Carbon	**CO_2**	12.15	10.49	16.66
Oxygen	**-**	59.29	61.14	52.83
Sodium	**Na_2O**	**-**	0.25	0.38
Magnesium	**MgO**	0.39	0.63	0.76
Aluminium	**Al_2O_3**	9.70	7.84	7.27
Silicon	**SiO_2**	14.77	14.76	16.27
Potassium	**K_2O**	1.35	1.69	2.01
Titanium	**TiO_2**	0.60	0.43	0.45
Iron	**Fe_2O_3**	1.76	2.77	3.37

Analysis of the overall chemical composition was obtained by SEM-EDS and is illustrated in Table 2 and X-ray diffraction (XRD) was also performed on the fine fraction (<2 µm) of the soils using the oriented aggregate mount method (Moore and Reynolds Jr, 1989) with a Bruker D8 Advance Diffractometer and a Cu Kα anode at an angle a range of 10° to 80°. The diffractograms are shown in Figures 3a – d where *a* is the untreated sample, *b* has been heated to 350°C, *c* has been heated to 550°C and *d* is the Ethyl Glycol treated sample. The results show that this fine

fraction of the soils is predominantly kaolinite and illite. However whilst kaolinite is dominant in soils U and W, soil V has a higher proportion of illite as well as containing vermiculite.

Fig. 3a XRD Diffractogram (Soil U)

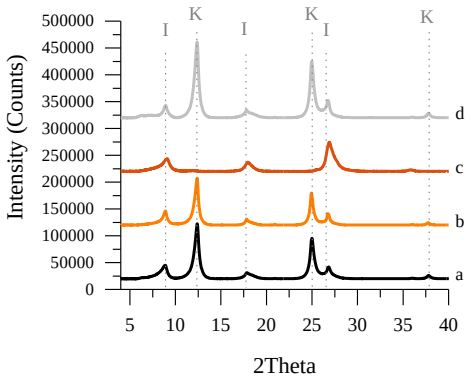


Fig. 3b XRD Diffractogram (Soil V)

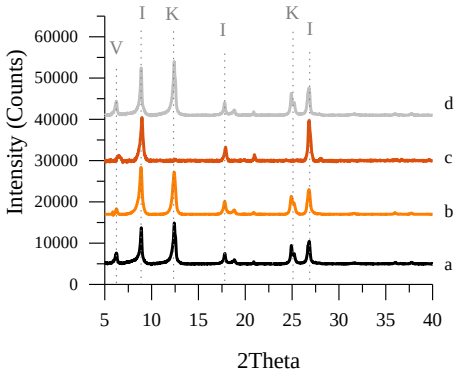
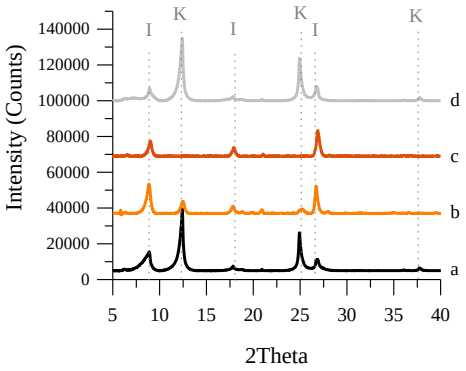


Fig. 3c XRD Diffractogram (Soil W)



3.1.2. Alginate Types

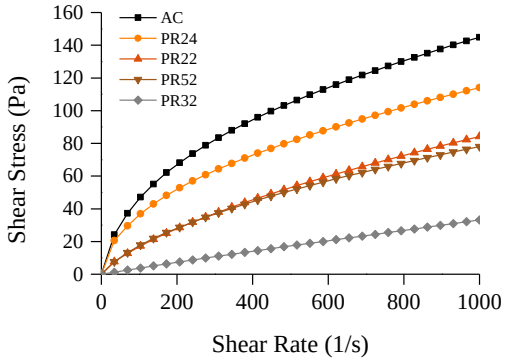
The alginate materials used in this study were sourced directly from a local manufacturer, Marine Biopolymers Ltd (MBL) and are derived from natural species of brown macro-algae found in Scotland's coastal environment, the most common of which are *Ascophyllum nodosum* and

Laminaria hyperborea (Burrows et al., 2010). Four different MBL products were utilised, including two *Laminaria hyperborea* stem products, one *Laminaria hyperborea* frond product and one *Ascophyllum nodosum*. A further commercial sample from Acros Organics was also used allowing a range of alginates from several seaweed sources and different properties to be studied (Table). The M/G ratios were provided by MBL and calculated using ^{1}H-NMR spectroscopy as per the methods of Grasdalen et al. (1979) and Davis et al. (2003). Viscosity measurements were conducted using a Brookfield R/S Rheometer with attached water bath to maintain a constant temperature of 25°C. Solutions of 1.0% alginate in 0.1 M NaCl were used to obtain flow curves for the different alginate types across a range of shear rates (Figure 4).

Table 3 Alginate Sources

Specimen	Source	M/G ratio	pH
PR22	L. hyperborea (stem)	1.04	8.2
PR24	L. hyperborea (stem)	0.23	6.7
PR32	L. hyperborea (frond)	0.72	5.4
PR52	Ascophyllum Nodosum	0.77	6.3
AC	Commercial Alginate	0.83	6.8

Fig. 4 Flow Curves of 1% Alginate Solutions



3.2. Specimen preparation

The specimens were produced using the experimental methodology of Galán-Marín et al. (2010) whereby soil, DI water and the desired sodium alginate product were mixed together in a 5L mechanical mixer. The amount of water for each mixture was calculated based on the optimum moisture content of the relevant soil. The sodium alginate was dissolved in the required amount of water and mixed using a magnetic stirrer for a minimum of 4 hours before being added to the dry soil. The material was then mixed for a period of approximately 3 minutes in order to produce a

homogenous mixture which could then be compacted into a steel mould to produce small-scale blocks (16 x 4 x 4cm) rather than full size bricks. The moulds were filled in two layers with each layer being compacted using 25 strokes of a tamper. The filled moulds were then oven dried at 50°C(±5°C) for 24 hours based on the prodecures adopted by Galán-Marín et al. (2010). After oven-drying, all samples were stored in a laboratory conditions at a temperature of approximately 18-21°C and a relative humidity range of 50%±10% for a minimum of 14 days. Unlike cement or lime stabilised materials which involve long term pozzolanic reactions, modification with biopolymers relies on more immediate effects such as crosslinking. Therfore the effect of longer curing times (eg 28 and 90 days) typically adopted for conventional stabilisers were not considered relevant at this stage. The same production procedure was used for the different batches with 3 specimens being produced for each batch. As shown in Table 4, a total of three soil types were studied including a control batch containing only soil and water. For soil V, an additional study investigating increased alginate dosages for selected alginate types was also included.

Table 4 Mix Compositions (16 x 4 x 4 cm specimen)

Specimen	Soil (g)	Alginate (g)	Water content (%)
U Samples	500g	0.5g	15%
V samples	500g	0.5g, 1.25g, 2.5g	16%
W samples	500g	0.5g	16%

3.3 Testing

3.3.1 General Properties

General observations were made regarding the workability of the mixture during preparation as well as the quality and homogeneity of the final specimens. Each block was also weighed and its dimensions measured. The unit mass (g) and unit volume (cm^3) were then used to calculate the bulk density (ρ). Comparisons of drying shrinkage were also made by comparing the length of the dry specimen with the initial mould dimensions.

3.3.2 Mechanical Strength

Although there are some existing guidance documents for earthen materials (Standards New Zealand, 1998;Walker, 2002;Government of New Mexico, 2009), there is a general lack of standardisation, particular regarding the mechanical testing of individual units. Procedures are

therefore often based on those used for concrete, blocks and fired bricks such as BS EN 772-1:2011, BS EN 772-6:2001, BS EN 1351:1997 and BS EN 1015-11:1999. Although these methods are not ideal, particularly where different geometries are being compared (Aubert et al., 2013; Aubert et al., 2015b), as discussed by Quagliarini and Orazio (2014) this can be accounted for through the use of appropriate correction factors and capping materials for example. There are however some discrepancies in the exact procedures used in existing studies regarding the mechanical behavior of earthen materials, with authors either ignoring platen restraint effects or using inconsistent corrections factors (Quagliarini and Orazio, 2014). For the purposes of this study where the objective is to compare specimens of the same size and compare with previous research using similar materials, the procedure adopted by Galán-Marín et al. (2010) was deemed appropriate.

3.3.3 Flexural Strength

A universal testing machine was first used to conduct 3 point bending test on the specimens in order to determine flexural strength. The bending test equipment consisted of two rollers on which the specimen rests with a gauge distance (l) of 100±5mm. A load was then applied gradually to an upper roller, rested on top of the specimen at the midpoint, using an Instron Universal Testing Machine at a rate of 1mm/min. The maximum load (F), width (b) and depth (d) were recorded for each specimen and used to calculate the flexural strength:

$$f = 1.5\frac{Fl}{bd^2} \quad (1)$$

Results were calculated to the nearest 0.01 N/mm^2 as an average of three specimens.

3.3.4 Compressive Strength

The 3 point bending test was then followed by compressive strength tests on the resulting half-blocks. The testing machine included two steel bearing plates and the specimens were capped using 3mm plywood as recommended by Walker (2004). The load was applied steadily at a rate of 2.5 mm/min until failure occurred and the maximum load (F_{max}) recorded. The compressive strength (σ) value for the specimens was then derived from F_{max} and the cross sectional area (A) of the specimen, and a minimum of three specimens were tested for each batch.

$$\sigma = F_{\max} \big/ A \quad (2)$$

Platen restraint effects were also considered by using a correction factor which accounts for variations in specimen geometries (Morel et al., 2007; Quagliarini and Orazio, 2014). Since the height to width ratio of the specimens is 1, in this case a correction factor of 0.58 (Heathcote and Jankulovski, 1992) was used and multiplied by F_{max} to give the unconfined compressive strength values.

3.3.5 Abrasive Strength Coefficient

Abrasive strength provides a measure of how well a material can withstand the impacts of mechanical erosion to its surface and is therefore a useful measurement of durability. The test involves applying a given number of strokes at a constant pressure to the material surface using a wire brush and measuring the difference in mass before and after brushing (Adam and Agib, 2001). For the purposes of this study, a wooden brush with metal bristles and a 2kg weight attached was used. After weighing the initial mass of the specimen (m_1), the brush was then used to abrade the surface of the sample using a standard procedure of 60 strokes. After brushing, any loose material was removed and the specimen was reweighed (m_2).The abrasive strength coefficient (C_a) was then calculated, taking into account the length of the specimen (L) and the width of the brush (w):

$$C_a = \frac{L \times w}{m_1 - m_2} \quad (3)$$

3.3.6 Hygroscopic Sorption Properties

The procedure for this test is based on ASTM C1498 − 04a and BS EN ISO 12571:2014 and involves placing the test material in environments of varying relative humidity (RH) and measuring the weight of moisture absorbed. Triplicate samples were oven-dried to constant mass (m_0) before being placed in a non-absorbent container with a tight fitting lid. A desiccator with an appropriate saturated salt solution was also prepared and allowed to equilibrate to the required relative humidity (RH). The specific salt solutions used were Potassium Acetate (CH_3COOK), Magnesium Nitrate ($Mg(NO_3)2{\cdot}6H_2O$), Sodium Chloride (NaCl) Potassium Chloride (KCl) and Potassium Nitrate (KNO_3), giving corresponding relative humidity values of 23%, 54%, 75%, 85% and 95% as derived from the standard values presented in BS EN ISO 12571:2014. The samples were then placed inside the desiccator with the lids removed. After 24 hours, the samples were removed from the desiccator and weighed immediately. This process of daily weighing's was repeated until 3 successive mass readings (m) showed a change in mass of less than 0.1%. The equilibrium moisture content (u) at the given RH was then calculated as an average of the three samples:

$$u = \frac{m - m_0}{m_0} \quad (4)$$

This process was then repeated for a minimum of 4 different RH values, working from low humidity to high humidity allowing isotherms showing the relationship between u and RH to be plotted.

3.3.7 Water Sensitivity

Assessment of the water stability of masonry materials is generally achieved by comparing the 'dry' compressive strength with the 'wet' compressive strength where specimens have been submerged in water. However, in the case of unfired materials, these tests are unsuitable since the material generally disintegrates upon direct contact with water. There are therefore currently no corresponding BS testing procedures for assessing the water absorption properties of unfired clay materials. Due to the fact that it is proposed that these materials would only be used in internal controlled environments, in this study the objective was to gain an initial assessment of the water sensitivity of the samples. An adapted version of the capillary absorption test (as described in BS EN 1015-18:2002 or BS EN 772-11:2011) was therefore developed in order to provide a less severe experiment than one requiring full submersion in water. The method adopted was designed to compare the behaviour of the specimens upon exposure to moisture on a single surface. This involved firstly drying the specimens to a constant mass and measuring the dimensions of the face which was to be immersed in water. A large tray was filled with DI water which included a supporting mesh material to ensure that the specimens did not touch the base of the container. The mesh permitted only 5 mm ± 1 mm of the specimen to be immersed in water and an immersion period of 60s was used for each sample. The water level was kept at the same level for the test duration. After immersion, the samples were oven dried for 24 hours allowing the difference in unit mass before (m_1) and after testing (m_1) to be calculated. This was then used to compare the percentage of material lost during the controlled exposure to water for each sample using equation 5 below.

$$\textit{Mass loss (\%)} = \frac{m_{1-}\, m_2}{m_1} \times 100 \qquad (5)$$

3.3.8 Microstructure (SEM)

A HITACHI S-3700 SW scanning electron microscope (SEM) was used to generate images of the fracture surface of the different samples. All of the samples were first cut into small fragments and sputter coated in gold prior to analysis.

4. Results and Discussion

A summary of the basic block (16 x 4 x 4 cm) properties are shown in Table 5, demonstrating bulk densities within the range of 1.8 – 2.1 g/cm^3.

Table 5 Summary of Block Properties

Specimen	Alginate Source	Average Bulk Density (g/cm^3)	Homogeneity (Good / Mod. / Poor)	Linear Shrinkage (%)
U	-	1.85±0.04	Mod.	5.6±0.0

PR22U	L.H. Stem	1.90±0.04	Good	4.2±0.3
PR24U	L.H. Stem	1.90±0.01	Good	5.0±0.0
PR32U	L.H. Frond	1.93±0.04	Good	4.0±1.0
PR52U	Asco.	1.90±0.04	Poor	3.3±0.4
ACU	Commercial	2.00±0.04	Poor	4.0±1.0
V	-	1.94±0.03	Mod.	5.4±0.3
PR22V	L.H. Stem	2.11±0.13	Good	6.9±0.6
PR24V	L.H. Stem	2.01±0.03	Good	5.0±0.0
PR32V	L.H. Frond	1.92±0.04	Good	5.2±0.3
PR52V	Asco.	2.02±0.01	Mod.	5.6±0.6
ACV	Commercial	1.99±0.06	Good	6.5±0.4
W	-	1.81±0.5	Mod.	2.7±0.6
PR22W	L.H. Stem	2.14±0.24	Mod.	5.2±0.4
PR24W	L.H. Stem	2.06±0.11	Mod.	5.0±0.0
PR32W	L.H. Frond	2.05±0.02	Mod.	4.2±0.3
PR52W	Asco.	1.98±0.14	Mod.	4.0±0.4
ACW	Commercial	2.01±0.06	Mod.	4.4±0.0

4.1 Flexural Strength

The results for the 3 point bending tests are shown in Figure 5. Based on ANOVA and a Tukey post-hoc test, only specimens PR22W, PR22U and ACV offered statistically significant improvements compared to the relevant controls at the $p<0.05$ level (denoted by *). The relatively high standard deviations highlight the variations in quality for specimens within the same batch. Overall soil W provided much lower values than the other 2 soil types. However, specimen PR22W offered the greatest increase in strength (an increase of 123% compared to the control mix) of all the specimens studied. Overall the range of values for soil U and V are comparable to the flexural results achieved by Galán-Marín et al. (2013), however this study additionally demonstrated the level of flexural strength increases compared to control samples. Interestingly, in the case of the dosage study, as shown in Figure 6, increasing the dosage of alginate added to the soil mix did not significantly improve the flexural strength of the blocks.

Fig. 5 Flexural Strength

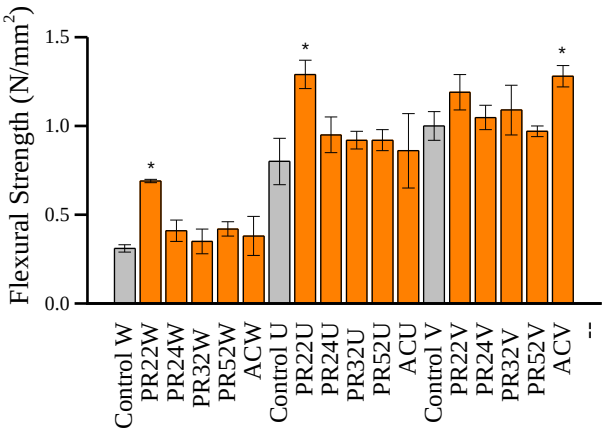
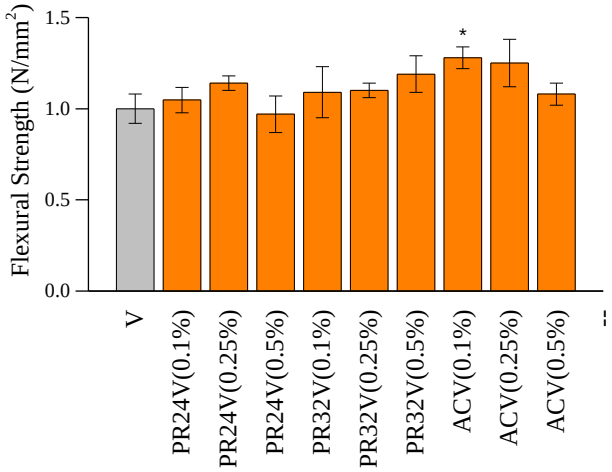


Fig. 6 Flexural Strength - Dosage Study

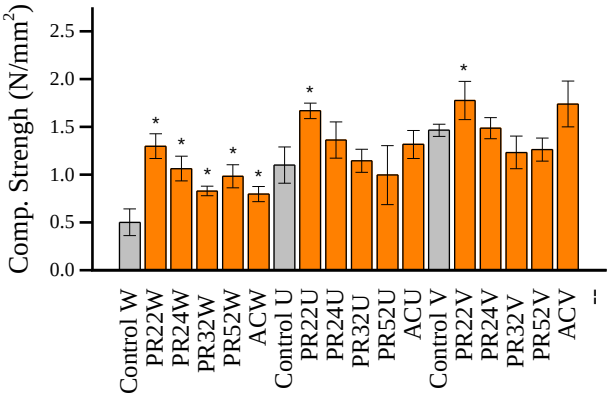


4.2 Compressive Strength

Previous research indicates that unfired clay bricks achieve compressive strength values of 1 – 4 N/mm^2 depending on parameters such as moisture content and density (Sutton et al., 2011). For the small scale blocks tested in this study, the values achieved before the application of a correction factor, were between 0.8 and 3 N/mm^2, with an average value of 2.1 N/mm^2 for a dry density range of 1.8 – 2.1 g/cm^3 and moisture contents of 1.0-2.5%. The unconfined compressive strength values shown in the graphs however were between 0.5 and 1.78 N/mm^2. As shown in Figure 7, PR22 once again offered the greatest improvement for all soil types. A maximum increase of strength was witnessed for PR22W where an improvement of over 160% was achieved. This is much greater than the maximum relative increases for samples of the same geometry witnessed by Galán-Marín et al. (2010) upon the addition of alginate alone. As a further comparison, Lee et al. (2008) observed a compressive strength increase of 15% using a 'seaweed glue' product and Achenza and Fenu (2006) demonstrate an improvement of ~75% using a

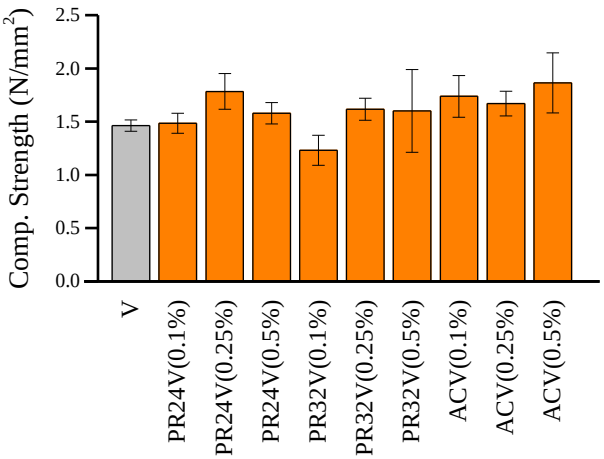
combination of seaweed fibres and biopolymer obtained from vegetable wastes, however it should be noted that both of these studies made use of cubic specimens. Results are also comparable to values reported for other biopolymers such as tannins which achieve a maximum strength of ~ 2 N/mm^2, offering improvements of 8% and 19% depending on the moisture content for cylindrical specimens (Sorgho et al., 2014). As shown in the flexural strength results, the soil type was clearly an important factor since all of the W specimens had the lowest values. However, whilst in the case of soil W all of the alginate types led to a visible improvement in strength, for soils U and V, only PR22 offered a statistically significant increase. Again there was high variability within some of the batches such as PR52U and ACU. Similar variations in compressive strength have been reported in other studies involving earthen materials, mainly due to the variable homogeneity of the samples (Aubert et al., 2015b).

Fig. 7 Compressive Strength



The dosage study performed with soil V indicated that increasing the alginate dosage did not lead to significant increases in strength (Figure 8). Although the dosage rates studied represent a small range, trials conducted using higher dosages indicated that even at a 1% dosage the material became unworkable and achieving a homogenous mix was very difficult. This suggests that the dosage range studied is within the practical range.

Fig. 8 Compressive Strength - Dosage Study



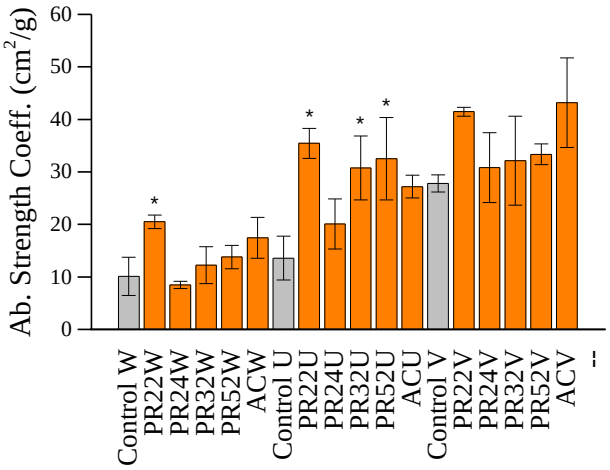
Overall the results from the mechanical strength tests indicate that, as expected, the strength properties of the blocks are closely linked with the base soil. On the other hand, the poorest soil, in mechanical strength terms, appears to be most affected by the addition of alginate as evidenced by the comparative magnitude of strength increases. This suggests that even this relatively small proportion of <2 μm particles (16%) is sufficient for interaction with the alginate to occur. Conversely, for soil U and V, the higher contents of 31% and 27% respectively appear to provide a sufficient amount of cohesive strength between the soil particles meaning that only certain types of alginate offer any further improvement. Although none of the samples passed the target compressive strength value of 2 N/mm^2 suggested by most existing standards (Jiménez Delgado and Guerrero, 2007), the strength values are somewhat limited by handmade nature of the specimens and it is anticipated that higher results could be achieved using alternative equipment. Indeed the final compressive strength values achieved by Galán-Marín et al. (2013), even for the control specimens, are greater than those observed in this study suggesting that differences in the production process, particularly in the compaction technique should be taken into account. The unconfined compressive strength results are also lower than the typical results reported for cement stabilised earth blocks depending on the cement content and product techniques used. For example Millogo and Morel (2012) report values of 4.5 – 6.5 N/mm^2 for cement dosages of 4-12%.

4.3 Abrasive Strength Coefficient

The abrasive strength tests (Figure 9) again show variable results however statistically significant improvements, compared to the control samples, are demonstrated in PR22W, PR22U, PR32U and PR52U. This suggests that for these samples the polymer is helping to promote stronger bonds between individual clay particles. Similar observations were also described by Atzeni et al. (2008) where a reduction in the amount of material abraded from the surface of earth bricks during sand-blasting was achieved using organic, polymeric stabilisers. In that study, the authors' attributed the

improvement to the formation of a protective polymer film, a mechanism which is not produced by typically inorganic stabilisers such as cement and lime (Atzeni et al., 2008).

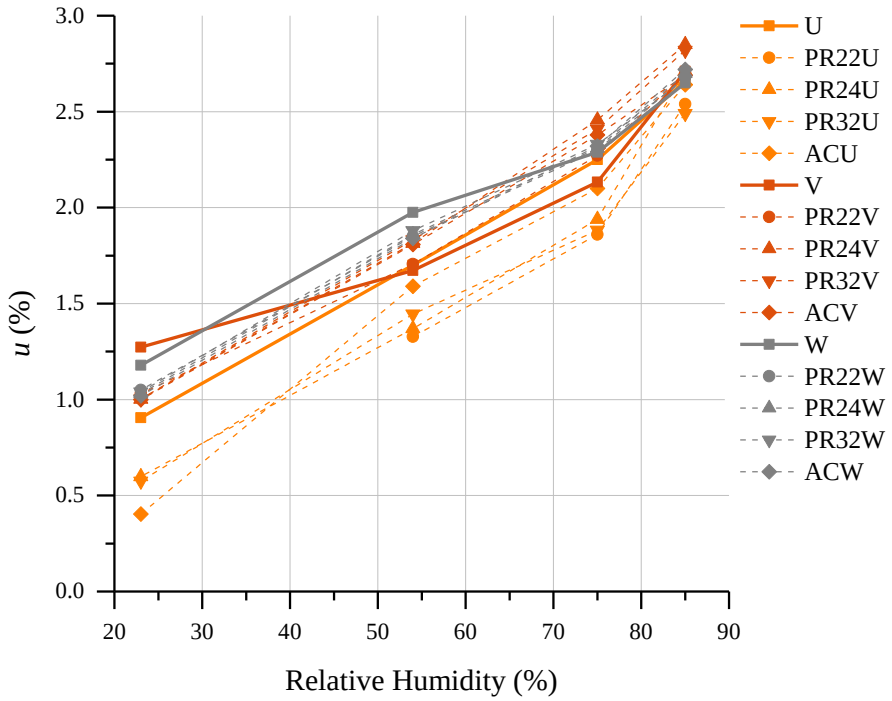
Fig. 9 Abrasive Strength Coefficient



4.4 Hygroscopic Sorption Properties

The absorption isotherms shown in Figures 10 demonstrate that all of the specimens absorb approximately 1-2.5% moisture at a normal indoor RH range of 40-60%. These results were slightly higher than those of Padfield and Jensen (2011) for unfired clay which absorbed approximately 0.8 – 1.3%. Nonetheless, the samples in this study appear to have a better sorption properties than common fired bricks and concrete which absorb 0 – 0.6% across the same RH range (Padfield and Jensen, 2011). The addition of alginate does not appear to drastically effect the sorption properties. This finding is in agreement with other studies which argue that the hygroscopic behaviour is linked primarily to the properties of the soil such as the particle size distribution and type of clay minerals present (McGregor et al., 2014b). Further investigation regarding the water vapour permeability and moisture buffering values would however be required before the humidity buffering behaviour could be fully characterised for the different clay-alginate combinations.

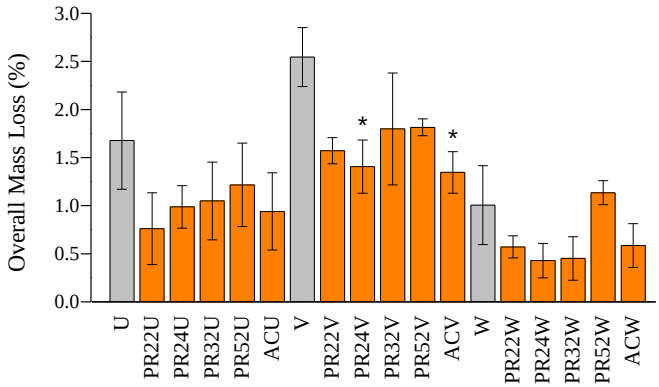
Fig. 10 Sorption Isotherms



4.5. *Water sensitivity*

In considering firstly the water stability tests, the overall mass loss for the samples upon exposure to water for a period of 60s is shown in Figure 11. Although only a few statistically significant results were observed in comparison to the control samples (PR24V and ACV), the test highlights the overall sensitivity of the samples, with and without the alginate, when the surface is directly exposed to moisture. Indeed all of the samples were found to lose between ~0.5 – 2.5% of their total mass due to the submerged portion of material disintegrating at the surface. Although there are some indications of a minor decrease in overall mass loss upon the addition of alginate, unlike other conventional stabilisers, it does not render the material impervious to water.

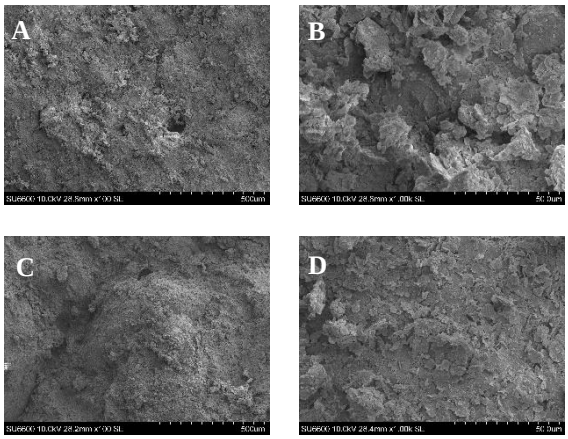
Fig. 11 Water Sensitivity – Overall Mass Loss



4.6 *Microstructure(SEM)*

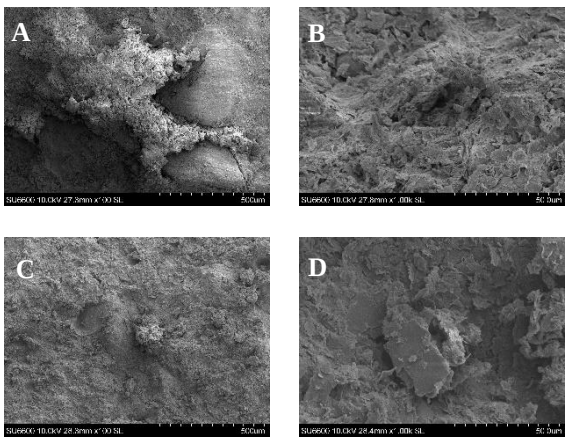
Selected SEM micrographs for the different soil types are shown in Figures 12 - 14. In most cases the control and alginate containing samples are relatively similar suggesting that this dosage of alginate does not dramatically affect the clay microstructure. All of the samples show aggregates of varying sizes however soil V appears to have a rougher, more irregular fracture surface compared to the soil W control sample. Clay bridges around the larger silt and sand particles can even be seen in some areas (Figure 14a). This is likely due to the higher content of clay sized particles within soil V which result in increased cohesion between the silt and sand particles (Attou et al., 1998), even without the addition of the alginate.

Fig. 12 SEM Micrographs (U)



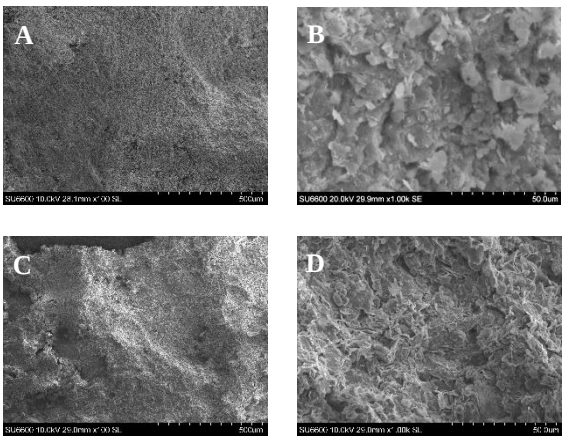
a) control U, x100; b) control U, x1000;
c) PR22U, x100; d) PR22U, x1000.

Fig. 13 SEM Micrograph (V)



a) control V, x100; b) control V, x1000;
c) PR22V, x100; d) PR22V, x1000.

Fig 14 SEM Micrograph (W)



a) control W, x100; b) control W, x1000;
c) PR22W, x100; d) PR22W, x1000.

4.7. Role of alginate/soil types

In order to explain these observations it is necessary to look more closely at the properties of the particular alginate sources as well as the differences between the three soil types. In the case of the alginates, PR22 and PR24 are both *Laminaria Hyperborea* stem products with different M/G ratios and different rheological behaviours . In theory, a higher viscosity, high molecular weight alginate would provide longer polymer chains and hence lead to more crosslinking sites per chain. However, a high viscosity can also have a negative impact since the tortuous nature of the long polymer chains can inhibit potential interactions between the polymer and the clay. Such results were observed by Pongjanyakul and Puttipipatkhachorn (2007) in aqueous sodium alginate/smectite systems where high viscosity alginates showed a weaker interaction than low viscosity alginates of the same M/G composition. This may explain why the commercial alginate (AC), which has a similar M/G composition to PR22 but a much higher viscosity, produces inconsistent results. It was also noted that during specimen production, the very high viscosity products, namely AC and PR24, inhibited mixing of the wet soil, consequently leading to less homogenous and poorer quality specimens and this may have contributed to the results. With regards to PR32 and PR52, although these alginates have similar G contents to PR22, they also have the lowest viscosities of all the products tested and it is therefore likely that the polymer chains are too small to impart improvements comparable with the other polymers.

In looking at the importance of the different soil types, properties such pH, cation concentration and the chemical composition can also influence the degree of interaction. Firstly, in the case of pH, it would be expected that soil U which is more acidic than the other soils would provide more favourable conditions for clay-polymer adsorption. However this was not apparent in these

particular tests and it was difficult to determine the importance of pH due to the complexity of other factors impacting on the clay-polymer interactions. In comparing the chemical composition of the soils, soils W and V both have a higher calcium content than that of soil U (Table 1). This perhaps explains why soil W demonstrates significant improvements since there is sufficient amount of calcium available to crosslink with the polymer. Although soil V also contains a relatively high quantity of calcium, the crosslinking effects of the alginate appear to be overshadowed by the existing cohesive bonding imparted by the greater fine fraction as evidenced by the high strength values of the control specimen. Walker (1995) recommends a clay content of 20-35% for effective stabilisation of earthen materials with cement and also reports that increases in clay content can reduce the effectiveness of any stabilising additives due to the formation clay aggregates during mixing. This supports the findings in this study that the magnitude of strength increases are lower for the high clay content soils.

Another parameter discussed by several authors relates to recommendations for the Atterberg limits of soils which are to be used for building purposes. Houben and Guillaud (1994) for example suggested a LL of 25-51% and a PI of 2-31% for compressed earth blocks. All of the soils used within this study fall within these ranges. The importance of PI is further highlighted in the conclusions of Galán-Marín et al. (2013) where it is proposed that success of the best performing soil is attributed to its high illite content (50%) and PI value (15.7%). In this study, the overall strength also appears to increase with increasing PI and illite content but this factor has been shown to have a negative impact on the percentage increase in strength when the alginate is added.

5. Conclusions

Alginate has the potential to be used as an additive for products like unfired earth bricks where increased particle bonding is desired. This study has improved understanding of the role of the alginate component in such materials, highlighting that increases in compressive strength - and in a more limited number of cases - flexural strength, can be achieved, but that the magnitude of these increases is dependent on both the type of alginate and the type of soil utilised. The most significant strength modification was witnessed when using a soil with a relatively low clay content, a sufficiently high calcium content and PI, combined with a medium viscosity alginate sourced from a *Laminaria Hyperborea* stem (PR22). For most of the other alginate types however, the compressive strengths achieved were comparable and in some cases lower than the equivalent control sample. This supports the conclusions of Nugent et al. (2009) that competing nano-scale interactions between polymers and clay particles contribute to overall strength changes. In this study it is therefore likely that in cases where there is an improvement in strength, as per the PR22 specimens, interactions which improve the strength of the soil structure such as biopolymer cross-linking or clay-polymer interactions are more dominant. Further investigation into the relative

importance of the different soil properties, including pH, calcium content and clay type/quantity, using more sensitive tests parameters, is recommended in order to further assess the role of the soil.

Although this study describes new evidence regarding alginate-clay interactions, the overall strength properties of the specimens studied are still relatively low compared to contemporary masonry materials such as fired bricks, concrete and cement or lime stabilized earth. Other strategies to improve the strength of the material such as the inclusion of an additional calcium source or the use of alternative compaction methods would therefore be required before the alginate-clay composite could be considered as a viable alternative for conventional load-bearing masonry. However, the material could be suitable in non-loadbearing applications such as infill within timber frames, where hygroscopic properties of the clay could be exploited for humidity regulation. In interpreting the results from the durability tests such as the abrasive strength and water sensitivity experiments, it was shown that only a few of the alginate containing samples offered any improvement over the controls. Despite this small number of statistically significant results, the overall durability is still a concern given that all of the samples were susceptible to considerable disintegration upon contact with water. While it may be argued that this issue may be mitigated through appropriate detailing or coatings (Morton, 2008), this still limits the use of the material to internal, protected applications. This also does not completely eradicate the risk of wetting and remains a concern for use in load-bearing walls (Heath et al., 2012). Further investigation of other properties such thermal performance, acoustic properties, water vapour transfer properties and long term durability would also need to be performed in order to fully evaluate the suitability of the specimens for commercial use.

Word Count: 8073

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